# Kinetics and mechanism of oxidation of ethyl- 2 - chloropropionate with potassium perm agnate in acidic medium

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**ABSTRACT**

The Kinetics of oxidation of ethyl 2-chloropropionate was carried out with oxidising agent KMnO4 in acidic medium the reaction was found in first order with respect to the concentration of substrate and its pseudo first order with respect to concentration of oxidant. Temperature also affect the rate of reaction as the temperature increase rate of reaction increase as well as concentration of acid affect the rate of reaction as the concentration of acid increases rate of reaction also increases and the study of mechanism show the formation of compound weather it is slow or fast.

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## Introduction

Among the various organic compounds employed in oxidative studies esters ethyl-2-chloropropionate attractive substrate in terms of their availability and easy to oxidative property. These compounds readily undergo oxidation with various oxidants. Kinetic studies constitute important source of mechanistic information about reaction.

During the oxidation by permanganate it is evident that the Mn (VII) in permanganate is reduced to various oxidation states in acid, alkaline and neutral media. The mechanism by which this multivalent oxidant oxidise a substrate depends not only on the substrate but also on medium used for the study in strongly alkaline medium the stable reduction product is the magnate ion, $MnO_4^{-2}$ requires a pH range 12-13$^{PH}$ below which the system becomes distributed and the reaction will proceed. Further to give a reduced product of oxidant as Mn (IV) which slowly develops yellow turbidity[1]?

Oxidation reaction by Potassium permangante is of considerable academic and technological importance because of variable oxidation state of potassium (k).

The Kinetics provides the useful information about the mechanism and rate of chemical reaction, which helps to run a Oxidation of organic compound carried out by oxidising agent like potassium dichromate Cr (VI)[2-4] The update literature survey shows that, though the considerable amount of work has been done on the oxidation of organic compounds[5to13] by potassium permanganate, but only a few studies is found on the kinetics of oxidation of ester by potassium permagnate[14,15]. The object of present investigation is to formulate the reaction mechanism from the date gathered from kinetic measurement. It is found that the oxidation of ester occurs by two ways, hydrolysis followed by the oxidation of alcohol, direct oxidation of esters. But no conclusive evidence was provided in support of either of the two pathways; hence it is decided to undertake the systematic investigation kinetic of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, ethyl formate, isobutyl chloroformate. The kinetic of oxidation of ester by potassium permagnate in moderately concentrate sulphuric and medium has been investigated.

**The rate law**

$$\frac{-d\left[Mn(VII)\right]}{dt} = k\left(Ester\right)\left[MnO_4\right]_{total}$$

The result obtained shows that the direct oxidation is the only process occurring under the applied conditions of experiments.

Although the considerable amount of work has been carried out on organic compounds by update literature survey shows that few work has been on ester that is why we have planned to carry out the work of ester i.e. ethyl 3-chloropropionate by KMnO4 .

## Material and methods:

All the chemicals used were of AR grade, specially potassium permanganate used were of AR grade and was prepared and estimated by standard method. Esters are of Zobo Chem. Ltd., and the boiling point of esters was confirmed.

The ester were always freshly distilled before used for the kinetic measurement permanganate and sulphuric acid solution were taken in two different flasks and covered with black cloth and placed in a thermostat for 1 hour to attain constant temperature by both the flask. In order to prevent the hydrolysis, required volume of given ester was directly added to acid solution with micro pipette just before mixing it with permanganate solution.

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The course of reaction was followed by measuring the absorbance (optical density) of unreacted permanganate ions from time to time at 520 nm using Carl-Zeiss spectrophotomer. The reaction was followed upto 70 to 85% completion and the product was identified as acid i.e. acetic acid and aldehyde by 2, 4 DNP tests 16. The aldehydes were obtained in 90% yield as estimated from their 2.4 DNP derivative. The addition of mercuric chloride to reaction system did not induce the precipitation of mercuric chloride showing that no free radicals are formed in the system12.

## Results and discussion

Under the conditions [ester] > [KMnO4] in 3.20 M. H2SO4. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on [KMnO4].( figure not shown), A Oxidation of esters depends on the concentration of potassium permanganate. This was also confirmed by verifying [KMnO4] which did not show any change in Pseudo First order constant (k1) value (Table .1). The reaction was also found to be first order in [ester] (Table 2). The rate of reaction increases with increases in [H2SO4]. (Table .3)

The effect of temperature was also studied at different temperature like 283K, 293K, 303K, 313K, 323K and 333K. It is shown in (Table .4) and it is clear that as temperature increases rate constant increases. Thermodynamic parameters such as H# S# G#, E E and A i.e. frequency factor were studies.

The negative values of entropy of activation shows that the intermediate transition state is rigid the relatively small values of $V$H and $V$S are consistent with the reaction generally proceeds through highly ionised transition state[17].

$$H^+ + MnO_4^{-2} \rightarrow HMnO_4^-$$
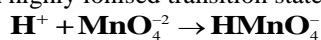
This point has been also confirmed by previous researchers. Hence Mn (VII) could be considered as the reactive specie and this probably exists to a certain extent as HMnO4.

As the acid concentration is increased the formation of HMnO4 is favoured and hence increases the oxidation may be assumed to be taking place by Mn (VII) in the form of either $MnO_4^-$ or *HMnO₄* or both depending on the acid concentration. The linear plot of 10K$^1$ Vs log [H$_2$SO$_4$] and logK$^1$ Vs Ho indicates that the reactions are acid catalyzed, but none of the above plots gives an ideal slope for unity. In view of the departure from the ideal behavior, applicability of Bunnett's hypothesis was tested. A plot of logK$^1$ Vs Ho Vs log H20 was linear (Fig not shown) and the slop was found to be -2.5. This value indicates non-involvement of water molecule in the rate determining steps as per Bennett's, while the hydrolysis rate was 3.2x10$^{-5}$ liter mol$^{-1}$ sec$^{-1}$ under identical condition, from this it is
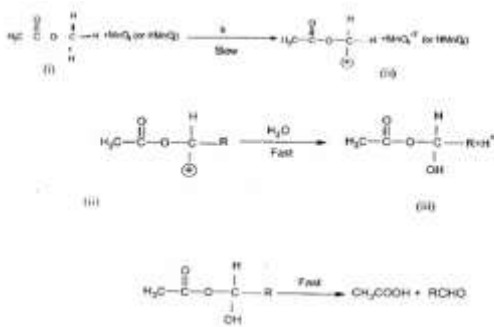


Compound (III) being highly unstable disproportionate to give acetic acid and the corresponding aldehyde. The rate law can be expressed by equation (1)

$$\frac{-d\left[Mn(VII)\right]}{dt} = k\left(Ester\right)\left[MnO_4\right]_{total}$$

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols etc. by permanganate in moderately concentrated acid solutions[18].

The effect of temperature on reaction rate was studied which shows the increase in reaction rate with increase in temperature (Table 4). The rate of oxidation in case of dimethyl phthalate, diethyl phthalate, and dibutylphthalate, the rate of reaction as the number of alkyl group increases there is decrease is clear that the direct oxidation is the only process occurring under the experimental conditions used.

A probable mechanism (scheme -1) in which $MnO_4^-$ or HMnO$_4$ attacks the alcohol moiety of the ester is consider explaining the observed kinetic result.

K value, due to steric effect In case of ethyl 3-chloropropionate and the rate of reaction is more though there is presence of electron with drawing group $C\bar{l}$ .

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**Table 1: Effect of variation of Oxidant (KMnO₄) [ Ethyl 2 - chloropropionate ] =**
**4.7 x 10⁻⁷ Temperature : 30°C $\lambda$ max = 520 nm**

| Sr.No. | [Oxidant]x10³ mol dm⁻³ | $K_{Obs}$ x 10² min.⁻¹ |
|---|---|---|
| *I* | 8.2 | 1.5 |
| *II* | 7.6 | 1.9 |
| *III* | 6.4 | 2.1 |
| *IV* | 5.2 | 2.2 |
| *V* | 4.8 | 2.3 |
| *VI* | 4.4 | 2.8 |
| *VII* | 3.1 | 3.2 |

*Table 2 : Effect of variation of Ethyl -2-chloropropionate*

| Sr.No. | [Substrate]x10² mol dm⁻³ | $K_{Obs}$ x 10² min.⁻¹ |
|---|---|---|
| *I* | 4.6 | 1.71 |
| *II* | 5.12 | 1.82 |
| *III* | 5.18 | 1.91 |
| *IV* | 7.26 | 2.10 |
| *V* | 8.64 | 2.22 |
| *VI* | 9.12 | 2.90 |
| *VII* | 10.21 | 3.1 |

**Table 3 : Effect of Concentration of [ H₂SO₄] on Oxidation of ethyl-2-Chloropropionate**

| Sr. No. | [acid]x10¹ mol dm⁻³ | Log [acid] | Kx 10³ min⁻¹ | Log K | Log $a_w$ | $H_O$ | $H_O$+Log K |
|---|---|---|---|---|---|---|---|
| I | 0.780 | -1.0794 | 1.11 | -1.952 | -0.0025 | 0.11 | -1.954500 |
| II | 1.42 | -0.7780 | 1.22 | -1.890 | -0.0050 | -1.50 | -3.390000 |
| III | 2.30 | -0.4770 | 1.41 | -1.820 | -0.0100 | -1.25 | -3.070000 |
| IV | 3.82 | 0.3803 | 1.64 | -1.770 | -0.0150 | -1.15 | -2.920000 |
| V | 4.64 | -0.3010 | 1.82 | -1.700 | -0.0175 | -1.00 | -2.700000 |
| VI | 5.82 | -0.1761 | 1.92 | -1.622 | -0.0200 | 0.90 | -2.522000 |
| VII | 7.62 | -0.0792 | 2.86 | -1.520 | -0.0250 | -0.60 | -2.120000 |

**Table 4 : Effect of variation of temperature an oxidation of ethyl-2- Chloropropionate**

| Tic | 1/T x 10⁻³ | logK | A | E J/Mole | $\Delta H \neq$ J/Mole | $VG \neq$ J/Mole | $\Delta S \neq$ J/Mole |
|---|---|---|---|---|---|---|---|
| 298 | 3.36 | -2.62 | 1.10 | 18124 | 15835 | 82011 | -219 |
| 303 | 3.30 | -2.42 | 1.12 | 18124 | 15740 | 82118 | -218 |
| 308 | 3.25 | -2.21 | 1.13 | 18124 | 15720 | 82214 | -219 |
| 313 | 3.19 | -1.91 | 1.18 | 18124 | 15540 | 82315 | -216 |
| 318 | 3.14 | -1.82 | 1.21 | 18124 | 15230 | 82437 | -217 |
| 323 | 3.10 | 1.61 | 1.22 | 18124 | 15112 | 82445 | -218 |

*Table 5 : Effect of variation of solvent*

| Sr.No. | [ % of solvent ] | $K_{Obs}$ min.⁻¹ |
|---|---|---|
| *I* | 10% | 0.0241 |
| *II* | 25% | 0.0198 |
| *III* | 30% | 0.0191 |
| *IV* | 40% | 0.0152 |
| *V* | 50% | 0.0128 |